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(54) NON-AQUEOUS ELECTROLYTE SECONDARY BATTERY AND MANUFACTURING METHOD

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain a non-aqueous electrolyte secondary battery having superior charge and discharge characteristics and less deterioration of discharge capacity due to charge and discharge repetition by containing a specific material in a negative pole and containing carbon dioxide in a nonaqueous electrolyte.
SOLUTION: In a non-aqueous secondary battery made of negative and positive poles containing a material capable of reversibly storing and discharging lithium, a non-aqueous electrolyte containing a lithium salt, and a separator, the negative pole contains a material made mainly of a non-crystal charcogen compound and/or non-crystal oxide including an atom of three or more types to be selected from 14 and 15 groups of periodic table and contains carbon dioxide in the non-aqueous electrolyte. Carbon dioxide contained in the non-aqueous electrolyte is 0.005mol/liter or more and 2mol/liter or less.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the high capacity nonaqueous electrolyte secondary battery excellent in the charge-discharge cycle characteristic.
a negative pole material -- mainly -- an amorphous charcogen compound -- and -- or it is related with improvement of charging and discharging characteristics, such as a charge-and-discharge cycle life etc. of a nonaqueous electrolyte secondary battery with big service capacity which is an amorphous oxide.

[0002]
[Description of the Prior Art]As a negative pole material for nonaqueous electrolyte secondary batteries, although a lithium metal and a lithium alloy are typical, Since it was the high activity which what is called a dendrite by which the lithium metal grew up to be arborescence generates, and the cause of an internal short or the dendrite itself has during charge and discharge when they are used, danger, such as ignition, had been entailed. On the other hand, nature material of baked carbon in which insertion and discharge are possible has come to be reversibly put in practical use in lithium. Since, as for a carbonaceous material, it being on a carbonaceous material in the case of a surcharge or boost charge in case a lithium metal's deposits since itself has conductivity, and also a carbonaceous material had comparatively low density, there was a fault that service capacity was restricted in the double meaning that the capacity per volume is low.
[0003]In recent years as what has the high discharge potential whose average discharge voltage is 3-3.6V class, and attains the nonaqueous electrolyte secondary battery of high capacity, Using oxides, such as Sn, V, Si, B, and Zr, and those multiple oxides for a negative pole material is proposed (JP,5-174818,A, 6-60867, 6-275267, 6-325765, 6-338324, and EP-No. 615296 each publication before examination). Oxides, such as these [Sn and V], Si, B, and Zr, and those multiple oxides, By combining with the anode of the transition metal compound containing a certain kind of lithium showed average discharge voltage of service capacity being large at 3-3.6V class, and there being almost no dendrite generating in a practical use field, and giving a nonaqueous electrolyte secondary battery with very high safety. However, also in these cells, there are problems, like depending on the handling of a negative pole material, a charging and discharging cycle receives restrictions, and stable manufacture and to improve a charge-discharge cycle characteristic further of the cell are desired.
[0004]
[Problem(s) to be Solved by the Invention]The technical problems of this invention are raising the charge-discharge cycle characteristic of a nonaqueous electrolyte secondary battery with big service capacity, and providing the stable manufacturing method of such a nonaqueous electrolyte secondary battery.
[0005]
[Means for Solving the Problem]In a negative electrode and an anode in which a technical problem of this invention includes for lithium material in which occlusion discharge is possible reversibly, nonaqueous electrolyte containing lithium salt, and a nonaqueous secondary battery which consists of separators, . This negative electrode contains three or more sorts of atoms chosen from the periodic tables 1, 2, 13, and 14 and 15 fellows atom. It was attained by nonaqueous electrolyte secondary battery making carbon dioxide contain in this nonaqueous electrolyte, and its manufacturing method, including material which mainly consists of an amorphous charcogen compound and/or an amorphous oxide.
[0006]
[Embodiment of the Invention]Although the desirable gestalt of this invention is lifted below, this invention is not

limited to these.
(1) In the nonaqueous electrolyte containing the negative electrode and the anode, and lithium salt which include for lithium the material in which occlusion discharge is possible reversibly, and the nonaqueous secondary battery which consists of separators, A nonaqueous electrolyte secondary battery, wherein this negative electrode makes carbon dioxide contain in this nonaqueous electrolyte, including the material containing three or more sorts of atoms chosen from the periodic tables 1, 2, 13, and 14 and 15 fellows atom which mainly consists of an amorphous charcogen compound and/or an amorphous oxide.
(2) A nonaqueous electrolyte secondary battery given in the paragraph 1, wherein the carbon dioxide contained in this nonaqueous electrolyte is 0.005 mol/l. or more 0.2 mol/l. or less.
(3) A nonaqueous electrolyte secondary battery given in the paragraph 1 or 2, wherein the supporting electrolytes contained in this nonaqueous electrolyte are $LiPF_6$ and/or $LiBF_4$ at least.
(4) A nonaqueous electrolyte secondary battery given in any 1 paragraph of the paragraphs 1-3, wherein this negative pole material is shown by a general formula (1).

$M^1M^2pM^4qM^6r$ general formula (1)

the inside of a formula, M^1, and M^2 -- difference -- Si, germanium, and Sn. A kind and M^4 that it is few as being chosen out of Pb, P, B, aluminum, and Sb Li, As for a kind, p, and q, 0.001-10r express the numbers 1.00-50 with a kind and M^6 being chosen from O, S, and Te as being chosen out of Na, K, Rb, Cs, Mg, Ca, Sr, and Ba, as it is few that it is few respectively.
[0007](5) In the nonaqueous electrolyte containing the negative electrode and the anode, and lithium salt which include for lithium the material in which occlusion discharge is possible reversibly, and the nonaqueous secondary battery which consists of separators, A manufacturing method of the nonaqueous electrolyte secondary battery characterized by making carbon dioxide contain in this nonaqueous electrolyte including the material containing three or more sorts of atoms in which this negative electrode is chosen from the periodic tables 1, 2, 13, and 14 and 15 fellows atom which mainly consists of an amorphous charcogen compound and/or an amorphous oxide.
(6) A manufacturing method of a nonaqueous electrolyte secondary battery given in the paragraph 5 using it making carbon dioxide content gas contact beforehand before pouring this nonaqueous electrolyte in this nonaqueous secondary battery.
(7) A manufacturing method of a nonaqueous electrolyte secondary battery given in the paragraph 5 or 6 contacting a cell in carbon dioxide content gas before [after pouring in nonaqueous electrolyte] obturation.
(8) A manufacturing method of a nonaqueous electrolyte secondary battery given in any 1 paragraph of the paragraphs 5-7 enclosing carbon dioxide content gas in a cell, and making carbon dioxide content gas contain within a cell after obturation at the time of obturation of this nonaqueous electrolyte secondary battery.
[0008]Enclosing carbon dioxide in a cell is known conventionally. For example, in a JP,7-176323,A publication before examination. It is indicated that it is useful to the prevention from generation of the lithium hydroxide coat which is a cell reaction inhibition thing to generate on the surface of a lithium metal or a lithium alloy negative electrode, By JP,7-249431,A and a 6-140077 publication before examination, when abnormalities, such as generation of heat, occur on a cell, in order to make a safety valve open wide certainly, it is indicated that built-in of the compound which generates carbon dioxide and carbon dioxide is effective. this invention persons -- the result of wholeheartedly research -- the amorphous charcogen compound of this invention -- and -- or it found out that dispersion in the charging and discharging cycle nature at the time of using an amorphous oxide for a negative pole material was improved by including the choke damp in an electrolysis solution etc., and resulted in the above-mentioned invention. When the above-mentioned negative pole material is used, consider the detailed powder of a negative pole material promoting disassembly of an electrolysis solution, or the unreacted raw material at the time of calcination depositing to negative pole material particles, and degrading a cycle characteristic as a cause by which a cycle characteristic varies, but. Existence of the choke damp does not understand the mechanism which prevents these.
[0009]A charge-discharge cycle characteristic can be raised without spoiling the high capacity of a nonaqueous electrolyte secondary battery by making nonaqueous electrolyte contain carbon dioxide in this invention. As a method of making carbon dioxide containing in nonaqueous electrolyte in this invention (dissolution), How to contact nonaqueous electrolyte in carbon dioxide content gas before pouring in in a cell, and to make it contain beforehand, Any of the method of contacting in carbon dioxide content gas after pouring in and before cell obturation, and making it contain and the method of enclosing carbon dioxide content gas in a cell at the time of cell obturation, and making carbon dioxide content gas contain within a cell after obturation may be sufficient,

and it can also be used combining these.

[0010]It can also be based on any of the method of introducing continuously through the method, the wetted wall column and the packed column, and bubbling tower which introduce carbon dioxide content gas by a batch type into nonaqueous electrolyte through an aeration pipe etc. as a method of contacting nonaqueous electrolyte to the choke damp beforehand. The method of making the carbon dioxide content gas pressurized within the pressure vessel contact is also effective.

[0011]As a method of making the choke damp contacting after pouring in and before cell obturation, Any of the method of introducing and contacting direct carbon dioxide content gas into the nonaqueous electrolyte in a cell, the method of introducing carbon dioxide content gas into the cell upper part, introducing carbon dioxide content gas by an electrolysis solution oil level, and making it contact, and the method of making application-of-pressure carbon dioxide content gas contact within a pressure vessel may be sufficient.

[0012]As a method of enclosing carbon dioxide content gas in a cell at the time of cell obturation, it is attained by obturating under a carbon dioxide content gas atmosphere. Although any of the mixed gas containing Junji gaseous carbon oxide and carbon dioxide may be sufficient as carbon dioxide content gas used for these, what does not contain moisture as much as possible is preferred, it is preferred that it is less than dew point-40 **, and it is preferred that it is especially below -50 **. As mixed gas, mixed gas with inactive gas, such as mixed gas with air, oxygen, etc., nitrogen, and argon, etc. can be used. As a quantity of the carbon dioxide made to contain in nonaqueous electrolyte, it is desirable in 0.005 mol/l. or more 0.2 mol/l. or less, and l. is [0.01 mol/l. / above] preferred in especially 0.1 mol /or less. The concentration of the carbon dioxide in an electrolysis solution can be measured by the GC method (the gas chromatography method). If too small, the effect to a charge-discharge cycle characteristic improvement is not enough, if there is too much quantity of carbon dioxide, at the time of use of a cell, problems, such as an inter-cell-pressure rise, occur by the rise of outside air temperature, and it is not preferred.

[0013]Generally an electrolysis solution comprises a supporting electrolyte dissolved in a solvent and its solvent, and its lithium salt (an anion and a lithium cation) is preferred. Solvent of the electrolysis solution which can be used by this invention As a solvent, Propylene carbonate, ethylene carbonate, butylene carbonate, Dimethyl carbonate, diethyl carbonate, methylethyl carbonate, Gamma-butyrolactone, methyl formate, methyl acetate, 1, 2-dimethoxyethane, A tetrahydrofuran, 2-methyltetrahydrofuran, dimethyl sulfoxide, 1,3-dioxolane, a formamide, dimethylformamide, dioxolane, Dioxane, acetonitrile, nitromethane, ethylmono- glyme, Trialkyl phosphate, trimethoxy methane, a dioxolane derivative, sulfolane, Aprotic organic solvents, such as 3-methyl-2-oxazolidinone, a propylene carbonate derivative, a tetrahydrofuran derivative, ethyl ether, and 1,3-propane Salton, can be mentioned, and these kinds or two sorts or more are mixed and used. The solvent of a carbonate system is preferred and that in which cyclic carbonate and/or non-cyclic carbonate were included is preferred in inside. As cyclic carbonate, ethylene carbonate and PUROPIRENKABONETO ** are preferred. As for non-cyclic carbonate and the bottom, it is preferred to include diethyl carbonate, dimethyl carbonate, and methylethyl carbonate.

[0014]As lithium salt which dissolves in these solvents that can be used by this invention, For example, $LiClO_4$, $LiBF_4$, $LiPF_6$, $LiCF_3SO_3$, $LiCF_3CO_2$, $LiAsF_6$, $LiSbF_6$, $LiB_{10}Cl_{10}$, Li salt, such as low-grade aliphatic-carboxylic-acid lithium, $LiAlCl_4$, LiCl, LiBr, LiI, chloroboranelithium, and 4 phenyl lithium borate, can be raised, and these kinds or two sorts or more can be mixed and used. What mixed a kind of $LiBF_4$, $LiPF_6$, and $LiCF_3SO_3$ or two sorts or more, and was dissolved especially is preferred. Especially the thing that mixed a kind of $LiBF_4$ and $LiCF_3SO_3$ or two sorts, and $LiPF_6$ is preferred. Although the concentration in particular of a supporting electrolyte is not limited, its 0.2-3 mol per l. of electrolysis solution is preferred. As an electrolysis solution which can be used by this invention, ethylene carbonate, propylene carbonate, The electrolysis solution which contains $LiCF_3SO_3$, $LiClO_4$, $LiBF_4$ and/, or $LiPF_6$ in the electrolysis solution which mixed suitably 1,2-dimethoxyethane, dimethyl carbonate, or diethyl carbonate is preferred. To a mixed solvent with propylene carbonate or ethylene carbonate, 1 and 2-dimethoxyethane and/, or diethyl carbonate, especially $LiCF_3SO_3$, The electrolysis solution containing $LiClO_4$, $LiBF_4$ and/, or $LiPF_6$ is preferred, and what contains ethylene carbonate and $LiPF_6$ at least especially is preferred. although the quantity in particular that adds these electrolysis solutions in a cell is not limited -- positive active material, the quantity of a negative pole material, and the size of a cell -- **** for initial complements -- things are made.

[0015]Hereafter, other materials and manufacturing methods for making the nonaqueous electrolyte secondary battery of this invention are explained in full detail. Right and the negative electrode used for the nonaqueous electrolyte secondary battery of this invention can paint positive electrode mixture or negative electrode

mixture on a charge collector, and can make it. A conducting agent, a binder, a dispersing agent, a filler, an ion conducting agent, a pressure enhancement agent, and various additive agents can be included in an anode or negative electrode mixture at each besides positive active material or a negative pole material, respectively.

[0016]As for the negative pole material used by this invention, it is preferred that it is mainly amorphous at the time of cell inclusion. That it is amorphous is a thing which has a broadcloth dispersion belt which has the peak from 20 degrees to 40 degrees with 2theta value with the X-ray diffraction method using CuK alpha rays said here, and it may mainly have a crystalline diffraction line. Among the crystalline diffraction lines preferably looked at by not less than 40 degrees 70 degrees or less with 2theta value, the strongest intensity, it is 100 or less times that they are 500 or less times of the diffraction line intensity of the peak of the broadcloth dispersion belt looked at by not less than 20 degrees 40 degrees or less with 2theta value desirable still more preferably, and they are 5 or less times especially preferably -- most -- desirable -- It is not having a crystalline diffraction line.

[0017]As for the negative pole material used by this invention, being expressed with a following general formula (1) is preferred.

$M^1M^2pM^4qM^6r$ general formula (1)

Among a formula, as being chosen out of Si, germanium, Sn, Pb, P, B, aluminum, and Sb in difference, M^1 and M^2 are kinds as it is few, they are Si, germanium, Sn, P, B, and aluminum preferably, and are Si, Sn, P, B, and aluminum especially preferably. As being chosen out of Li, Na, K, Rb, Cs, Mg, Ca, Sr, and Ba, M^4 is a kind as it is few, it is K, Cs, Mg, and Ca preferably, and is Cs and Mg especially preferably. As being chosen out of O, S, and Te, M^6 is a kind as it is few, it is O and S preferably, and is O especially preferably. p q is 0.001-10 respectively, is 0.01-5 preferably, and is 0.01-2 especially preferably. r is 1.00-50, is 1.00-26 preferably, and is 1.02-6 especially preferably. The valence in particular of M^1 and M^2 may not be limited, and may be an independent valence, or may be a mixture of each valence. In the range of 0.001 to 10 mol equivalent, M^2 and M^4 can change the ratio of M^1, M^2, and M^4 continuously to M^1, and the quantity (in a general formula (1), it is a value of r) of M^6 also changes continuously according to it.

[0018]Also in the above mentioned compound, in this invention, the case where M^1 is Sn is preferred and is expressed with a general formula (2).

$SnM^3pM^5qM^7r$ general formula (2)

Among a formula, as being chosen out of Si, germanium, Pb, P, B, and aluminum, M^3 is a kind as it is few, it is Si, germanium, P, B, and aluminum preferably, and is Si, P, B, and aluminum especially preferably. As being chosen out of Li, Na, K, Rb, Cs, Mg, Ca, Sr, and Ba, M^5 is a kind as it is few, it is Cs and Mg preferably, and is Mg especially preferably. As being chosen out of O and S, M^7 is a kind as it is few, and it is O preferably. p q is 0.001-10 respectively, is 0.01-5 preferably, is 0.01-1.5 still more preferably, and is 0.7-1.5 especially preferably. r is 1.00-50, is 1.00-26 preferably, and is 1.02-6 especially preferably.

[0019]Although the example of the negative pole material of this invention is shown below, this invention is not limited to these. $SnAl_{0.4}B_{0.5}P_{0.5}K_{0.1}O_{3.65}$, $SnAl_{0.4}B_{0.5}P_{0.5}Na_{0.2}O_{3.7}$, $SnAl_{0.4}B_{0.3}P_{0.5}Rb_{0.2}O_{3.4}$, $SnAl_{0.4}B_{0.5}P_{0.5}Cs_{0.1}O_{3.65}$, $SnAl_{0.4}B_{0.5}P_{0.5}K_{0.1}$germanium$_{0.05}O_{3.85}$, $SnAl_{0.4}B_{0.5}P_{0.5}K_{0.1}Mg_{0.1}$germanium$_{0.02}O_{3.83}$, $SnAl_{0.4}B_{0.4}P_{0.4}O_{3.2}$, $SnAl_{0.3}B_{0.5}P_{0.2}O_{2.7}$, $SnAl_{0.3}B_{0.5}P_{0.2}O_{2.7}$, $SnAl_{0.4}B_{0.5}P_{0.3}Ba_{0.08}Mg_{0.08}O_{3.26}$, $SnAl_{0.4}B_{0.4}P_{0.4}Ba_{0.08}O_{3.28}$, $SnAl_{0.4}B_{0.5}P_{0.5}O_{3.6}$, $SnAl_{0.4}B_{0.5}P_{0.5}Mg_{0.1}O_{3.7}$.

[0020]$SnAl_{0.5}B_{0.4}P_{0.5}Mg_{0.1}F_{0.2}O_{3.65}$, $SnB_{0.5}P_{0.5}Li_{0.1}Mg_{0.1}F_{0.2}O_{3.05}$, $SnB_{0.5}P_{0.5}K_{0.1}Mg_{0.1}F_{0.2}O_{3.05}$, $SnB_{0.5}P_{0.5}K_{0.05}Mg_{0.05}F_{0.1}O_{3.03}$, $SnB_{0.5}P_{0.5}K_{0.05}Mg_{0.1}F_{0.2}O_{3.03}$, $SnAl_{0.4}B_{0.5}P_{0.5}Cs_{0.1}Mg_{0.1}F_{0.2}O_{3.65}$, $SnB_{0.5}P_{0.5}Cs_{0.05}Mg_{0.05}F_{0.1}O_{3.03}$, $SnB_{0.5}P_{0.5}Mg_{0.1}F_{0.1}O_{3.05}$, $SnB_{0.5}P_{0.5}Mg_{0.1}F_{0.2}O_3$, $SnB_{0.5}P_{0.5}Mg_{0.1}F_{0.06}O_{3.07}$, $SnB_{0.5}P_{0.5}Mg_{0.1}F_{0.14}O_{3.03}$, $SnPBa_{0.08}O_{3.58}$, $SnPK_{0.1}O_{3.55}$, $SnPK_{0.05}Mg_{0.05}O_{3.58}$, $SnPCs_{0.1}O_{3.55}$, $SnPBa_{0.08}F_{0.08}O_{3.54}$, $SnPK_{0.1}Mg_{0.1}F_{0.2}O_{3.55}$, $SnPK_{0.05}Mg_{0.05}F_{0.1}O_{3.53}$, $SnPCs_{0.1}Mg_{0.1}F_{0.2}O_{3.55}$, $SnPCs_{0.05}Mg_{0.05}F_{0.1}O_{3.53}$.

[0021]$Sn_{1.1}$aluminum$_{0.4}B_{0.2}P_{0.6}Ba_{0.08}F_{0.08}O_{3.54}$, $Sn_{1.1}$aluminum$_{0.4}B_{0.2}P_{0.6}Li_{0.1}K_{0.1}Ba_{0.1}F_{0.1}O_{3.65}$, $Sn_{1.1}$aluminum$_{0.4}B_{0.4}P_{0.4}Ba_{0.08}O_{3.34}$, $Sn_{1.1}$aluminum$_{0.4}PCs_{0.05}O_{4.23}$, $Sn_{1.1}$aluminum$_{0.4}PK_{0.05}O_{4.23}$, $Sn_{1.2}$aluminum$_{0.5}B_{0.3}P_{0.4}Cs_{0.2}O_{3.5}$, $Sn_{1.2}$aluminum$_{0.4}B_{0.2}P_{0.6}Ba_{0.08}O_{3.68}$, $Sn_{1.2}$aluminum$_{0.4}B_{0.2}P_{0.6}Ba_{0.08}F_{0.08}O_{3.64}$, $Sn_{1.2}$aluminum$_{0.4}B_{0.2}P_{0.6}Mg_{0.04}Ba_{0.04}O_{3.68}$, $Sn_{1.2}$aluminum$_{0.4}B_{0.3}P_{0.5}Ba_{0.08}O_{3.58}$, $Sn_{1.3}$aluminum$_{0.3}B_{0.3}P_{0.4}Na_{0.2}O_{3.3}$,

$Sn_{1.3}aluminum_{0.2}B_{0.4}P_{0.4}Ca_{0.2}O_{3.4}$, $Sn_{1.3}aluminum_{0.4}B_{0.4}P_{0.4}Ba_{0.2}O_{3.6}$, $Sn_{1.4}aluminum_{0.4}PK_{0.2}O_{4.6}$, $Sn_{1.4}aluminum_{0.2}Ba_{0.1}PK_{0.2}O_{4.45}$, $Sn_{1.4}aluminum_{0.2}Ba_{0.2}PK_{0.2}O_{4.6}$, $Sn_{1.4}aluminum_{0.4}Ba_{0.2}PK_{0.2}Ba_{0.1}F_{0.2}O_{4.9}$, $Sn_{1.4}aluminum_{0.4}PK_{0.3}O_{4.65}$, $Sn_{1.5}aluminum_{0.2}PK_{0.2}O_{4.4}$, $Sn_{1.5}aluminum_{0.4}PK_{0.1}O_{4.65}$, $Sn_{1.5}aluminum_{0.4}PCs_{0.05}O_{4.63}$, $Sn_{1.5}aluminum_{0.4}PCs_{0.05}Mg_{0.1}F_{0.2}O_{4.63}$.

[0022]$SnSi_{0.5}aluminum_{0.1}B_{0.2}P_{0.1}Ca_{0.4}O_{3.1}$, $SnSi_{0.4}aluminum_{0.2}B_{0.4}O_{2.7}$, $SnSi_{0.5}aluminum_{0.2}B_{0.1}P_{0.1}Mg_{0.1}O_{2.8}$, $SnSi_{0.6}aluminum_{0.2}B_{0.2}O_{2.8}$, $SnSi_{0.5}aluminum_{0.3}B_{0.4}P_{0.2}O_{3.55}$, $SnSi_{0.5}aluminum_{0.3}B_{0.4}P_{0.5}O_{4.30}$, $SnSi_{0.6}aluminum_{0.1}B_{0.1}P_{0.3}O_{3.25}$, $SnSi_{0.6}aluminum_{0.1}B_{0.1}P_{0.1}Ba_{0.2}O_{2.95}$, $SnSi_{0.6}aluminum_{0.1}B_{0.1}P_{0.1}Ca_{0.2}O_{2.95}$, $SnSi_{0.6}aluminum_{0.4}B_{0.2}Mg_{0.1}O_{3.2}$, $SnSi_{0.6}aluminum_{0.1}B_{0.3}P_{0.1}O_{3.05}$, $SnSi_{0.6}aluminum_{0.2}Mg_{0.2}O_{2.7}$, $SnSi_{0.6}aluminum_{0.2}Ca_{0.2}O_{2.7}$, $SnSi_{0.6}aluminum_{0.2}P_{0.2}O_3$ and $SnSi_{0.6}B_{0.2}P_{0.2}O_3$, $SnSi_{0.8}aluminum_{0.2}O_{2.9}$, $SnSi_{0.8}aluminum_{0.3}B_{0.2}P_{0.2}O_{3.85}$, $SnSi_{0.8}B_{0.2}O_{2.9}$, $SnSi_{0.8}Ba_{0.2}O_{2.8}$, $SnSi_{0.8}Mg_{0.2}O_{2.8}$, $SnSi_{0.8}Ca_{0.2}O_{2.8}$, $SnSi_{0.8}P_{0.2}O_{3.1}$.

[0023]$Sn_{0.9}Mn_{0.3}B_{0.4}P_{0.4}Ca_{0.1}Rb_{0.1}O_{2.95}$, $Sn_{0.9}Fe_{0.3}B_{0.4}P_{0.4}Ca_{0.1}Rb_{0.1}O_{2.95}$, $Sn_{0.8}Pb_{0.2}Ca_{0.1}P_{0.9}O_{3.35}$, $Sn_{0.3}germanium_{0.7}Ba_{0.1}P_{0.9}O_{3.35}$, $Sn_{0.9}Mn_{0.1}Mg_{0.1}P_{0.9}O_{3.35}$, $Sn_{0.2}Mn_{0.8}Mg_{0.1}P_{0.9}O_{3.35}$, $Sn_{0.7}Pb_{0.3}Ca_{0.1}P_{0.9}O_{3.35}$, $Sn_{0.2}germanium_{0.8}Ba_{0.1}P_{0.9}O_{3.35}$[0024]The chemical formula of the compound produced by above-mentioned being calcinated is computable from the weight differences of the granular material before and behind calcination as inductively-coupled-plasma (ICP) emission spectrochemical analysis and a shortcut method as a measuring method. 50-700-mol% per negative pole material of the light metal insertion amount to the negative pole material of this invention is easy to be until it approximates it to the deposition potential of the light metal, but although it is desirable, it is especially desirable, for example. [100-600-mol% of] Many the burst sizes are so preferred that there are to an insertion amount. The insertion method of a light metal has electrochemical and the preferred chemical and thermal method. The electrochemical process of the method of inserting electrochemically the light metal contained in positive active material or the method of inserting in direct electrochemistry from a light metal or its alloy is preferred. The chemical method has the method of making it react to mixing with a light metal, contact, or an organic metal, for example, butyl lithium etc. An electrochemical process and the chemical method are preferred. This especially light metal has lithium or a preferred lithium ion.

[0025]In this invention, the nonaqueous electrolyte secondary battery safety was high at high discharge voltage and high capacity, and the high-electric-current characteristic excelled [nonaqueous electrolyte secondary battery] in it and the charge-discharge cycle characteristic was more excellent in the general formula (1) and (2) as shown above by using the compound shown mainly as a negative pole material can be obtained. In this invention, the outstanding effect's especially being acquired is using the compound which contains Sn and in which the valence of Sn exists with divalent as a negative pole material. It can ask for the valence of Sn by chemical titration operation. For example, it can analyze by the method of a statement to 165 pages of Physics and Chemistry of Glasses Vol.8 No.4 (1967). It is also possible to determine from the Knight shift by solid-state-nuclear-magnetic-resonance (NMR) measurement of Sn. For example, in broad measurement, metal Sn (zerovalent Sn) appears near -600 ppm near 100 ppm and in SnO_2 (= tetravalence) at SnO (= divalent) to a peak appearing in a lower field extremely with near 7000 ppm to $Sn(CH_3)_4$. Thus, since a Knight shift is greatly dependent on the valence of Sn which is a central metal when it has the same ligand, the determination of a valence is attained in the peak position required in ^{119} Sn-NMR measurement.

[0026]Various compounds can be included in the negative pole material of this invention. for example, a transition metal (Sc, Ti, V, Cr, Mn, Fe, Co, and nickel.) Cu, Zn, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, lanthanoid series metal, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, and periodic table 17 group element (F, Cl) can be included. The dopant of the various compounds (for example, compound of Sb, In, and Nb) which raise electron conductivity may also be included. 0-20-mol% of the quantity of the compound to add is desirable.

[0027]The synthetic method of the multiple oxide which makes a subject the oxide shown by the general formula (1) and (2) in this invention can adopt the calcinating method and any method of a solution technique. For example, what is necessary is to mix M^1 compound, M^2 compound, and M^4 compound (as for M^1 and M^2, Si, germanium, Sn, Pb, P, B, aluminum, Sb, and M^4 are Mg, Ca, Sr, and Ba in difference), and just to make it calcinate, when the calcinating method is explained in detail. As an Sn compound, for example, SnO, SnO_2, and Sn_2O_3, Sn_3O_4, Sn_7O_{13}andH_2O, Sn_8O_{15}, the first tin of hydroxylation, the second tin of oxy hydroxylation, Stannous acid, tin, the first tin of phosphoric acid, alt.stannic acid, metastannic acid, Para stannic acid, tin, the second tin of fluoridation, stannous chloride, a stannic chloride, the first tin of pyrophoric acid, Lynn-ized tin, the first tin of sulfuration, a tin bisulfide, etc. can be mentioned. As an Si compound, for example, SiO_2, SiO, a

tetramethylsilane, Hydro-silane compounds, such as alkoxy silane compounds, such as organosilicon compounds, such as a tetraethyl silane, a tetramethoxy silane, and a tetraethoxysilane, and trichloro hydro-Silang, can be mentioned. As a germanium compound, alkoxy germanium compounds, such as for example, GeO_2, GeO, a germaniumtetramethoxide, and germaniumtetraethoxide, etc. can be mentioned.
[0028]As a Pb compound, PbO_2 [for example,], PbO, Pb_2O_3, and Pb_3O_4, a lead nitrate, lead carbonate, lead formate, lead acetate, a lead tetraacetate, tartaric acid lead, lead diethoxide, lead JI (isopropoxide), etc. can be mentioned. As a P compound, diphosphorus pentaoxide, phosphorus oxychloride, phosphorous pentachloride, a phosphorus trichloride, phosphorus tribromide, trimethyl phosphoric acid, triethylphosphoric acid, TORIPURO pill phosphoric acid, the first tin of pyrophoric acid, phosphoric acid boron, etc. can be mentioned. As a B compound, for example, 32 boron oxide, boron trichloride, boron tribromide, boron carbide, way acid, way acid trimethyl ** way acid triethyl, tripropyl borate, way acid tributyl, boron phosphide, phosphoric acid boron, etc. can be mentioned. As an aluminum compound, for example, an aluminum oxide (alpha-alumina, beta-alumina), Aluminum silicate, aluminum tri-iso-propoxide, tellurous acid aluminum, An aluminium chloride, aluminum boride, aluminium phosphide, aluminium phosphate, aluminum lactate, way acid aluminum, aluminum sulfate, aluminum sulfate, aluminum boride, etc. can be mentioned. Antimony trioxide, triphenylantimony, etc. can be mentioned as a Sb compound. As Mg, Ca, Sr, and a Ba compound, each oxidation salt, a hydroxylation salt, carbonate, an phosphate, sulfate, a nitrate, an aluminium compound, etc. can be mentioned.
[0029]As a firing condition, it is not less than 6 ** 2000 ** or less that it is a not less than 4 **/m heating rate of 2000 ** or less as a heating rate desirable still more preferably. It is especially preferably preferred that it is 2000 ** or less, and is [not less than 10 **] not less than 250 ** 1500 ** or less as calcination temperature, It is not less than 350 ** 1500 ** or less still more preferably, and is not less than 500 ** 1500 ** or less especially preferably, And it is preferred that it is 100 or less hours as firing time for 0.01 hour or more, It is 70 or less hours still more preferably for 0.5 hour or more, and is 20 or less hours especially preferably for 1 hour or more, And it is below not less than 4 **107 ** that it is below not less than 2 **/m 107 ** as a temperature falling speed desirable still more preferably, and it is below not less than 6 **107 ** especially preferably, and is below not less than 10 **107 ** especially preferably. The heating rate in this invention is the mean velocity of a rise in heat until it reaches "80% of calcination temperature (** display)" from "50% of calcination temperature (** display)", The temperature falling speed in this invention is the mean velocity of a temperature reduction until it reaches "50% of calcination temperature (** display)" from "80% of calcination temperature (** display)."
[0030]It may cool all over a firing furnace and a temperature fall is taken out outside a firing furnace again, for example, may be supplied underwater and may be cooled. the gun method and the Hammer-Anvil method given in 217 pages of ceramic processing (Gihodo Shuppan 1987) -- rapid quenching, such as the -slap method, a gas atomizing method, the plasma-spraying method, a centrifugal quenching method, and the melt drag method, can also be used. It may cool using the single roller method given in 172 pages of new glass handbooks (Maruzen 1991), and the congruence roller method. In the case of the material fused during calcination, fired material may be taken out continuously, supplying a raw material during calcination. It is preferred to stir melt in the case of the material fused during calcination. Oxygen content is the atmosphere below 5 volume % preferably, and a calcination gas atmosphere is an inert gas atmosphere still more preferably. Nitrogen, argon, helium, krypton, a xenon, etc. are mentioned as inactive gas.
[0031]As for the mean grain size of the compound shown by the general formula (1) and (2) used by this invention, 1.0-30 micrometers is preferred, and especially its 2.0-20 micrometers are preferred. In order to use predetermined grain size, the grinder and classifier which were known well are used. For example, a mortar, a ball mill, a sand mill, a vibration ball mill, a satellite ball mill, a planetary ball mill, a turning air stream type jet mill, a screen, etc. are used. The wet milling which made organic solvents, such as water or methanol, live together at the time of grinding can also be performed if needed. It is preferred to perform a classification, in order to consider it as desired particle diameter. As the classification method, there is no limitation in particular and a screen, a pneumatic elutriation machine, an elutriation, etc. can be used if needed. Dry type and a wet type can use a classification. In especially this invention, it is preferred to remove 1 micrometer or less of detailed powder as much as possible. The fine fragmentation to mix is 1% or less more preferably 3% or less in a volume fraction. In order to remove an unreacted raw material etc. from the above-mentioned negative pole material particles, these particles may be rinsed or an organic solvent and a hydrous organic solvent may wash. The pH may be adjusted by salts with suitable water and organic solvent.
[0032]Rather than used by this invention as a desirable lithium containing transition metal oxide positive electrode material, It is preferred to mix and compound so that the mole ratio of the sum total of a lithium

compound/transition metal compound (at least one sort chosen from Ti, V, Cr, Mn, Fe, Co, nickel, Mo, and W with a transition metal here) may be set to 0.3-2.2. As a lithium containing transition metal oxide positive electrode material desirable for using and solving by this invention, It is preferred to mix and compound so that the mole ratio of the sum total of a lithium compound/transition metal compound (at least one sort chosen from V, Cr, Mn, Fe, Co, and nickel with a transition metal here) may be set to 0.3-2.2. It is preferred that lithium containing transition metal oxide positive electrode materials desirable for using and solving by this invention are Li_xQO_y (Q is mainly the transition metal in which a kind contains Co, Mn, nickel, V, and Fe at least here), x= 0.2-1.2, and y= 1.4-3. As Q, aluminum, Ga, In, germanium, Sn, Pb, Sb, Bi, Si, P, B, etc. may be mixed in addition to a transition metal. 0-30-mol% of a mixed amount is desirable to a transition metal.

[0033]Furthermore it is used by this invention, as a desirable lithium contained metal oxide positive electrode material, Li_xCoO_2, Li_xNiO_2, Li_xMnO_2, $Li_xCo_anickel_{1-a}O_2$, $Li_xCo_bV_{1-b}O_z$, $Li_xCo_bFe_{1-b}O_2$, $Li_xMn_2O_4$, $Li_xMn_cCo_{2-c}O_4$, $Li_xMn_cnickel_{2-c}O_4$, $Li_xMn_cV_{2-c}O_4$, $Li_xMn_cFe_{2-c}O_4$ (it is x= 0.7-1.2, a= 0.1 to 0.9, b= 0.8 to 0.98, c= 1.6-1.96, and z= 2.01-2.3 here) is raised. As most desirable lithium containing transition metal oxide positive electrode material used by this invention, Li_xCoO_2, Li_xNiO_2, Li_xMnO_2, $Li_xCo_anickel_{1-a}O_2$, $Li_xMn_2O_4$ and $Li_xCo_bV_{1-b}O_2$ (it is x= 0.7-1.2, a= 0.1 to 0.9, b= 0.9 to 0.98, and z= 2.01-2.3 here) are raised. Here, the above-mentioned x value is a value before a charge-and-discharge start, and is fluctuated by charge and discharge.

[0034]It is [anything] good if it is a electron conductive material which does not cause a chemical change in the constituted cell as conductive carbon compounds which can be used by this invention. As an example, natural graphite, such as flaky graphite, scaly graphite, and earthy graphite, petroleum coke, High-temperature-firing objects, such as coal corks, cellulose, sugars, and a mesophase pitch, Graphite, such as artificial graphites, such as vapor-phase-epitaxy black lead, acetylene black, Carbon black, such as furnace black, Ketchen black, channel black, lamp black, and thermal black, an asphalt pitch, coal tar, activated carbon, a meso fuze pitch, poly acene, etc. can be raised. In these, graphite and carbon black are preferred. As conducting agents other than a carbon system, independent or these mixtures can be included for conductive metallic oxide, such as conductive whiskers, such as metal powders, such as conductive fibers, such as a metal fiber, copper, nickel, aluminum, and silver, a zinc oxide, and potassium titanate, and titanium oxide, etc. if needed. As for the addition to the binder layer of a conducting agent, it is preferred that it is 6 to 50 % of the weight to a negative pole material or a positive electrode material, and it is especially preferred that it is 6 to 30 % of the weight. Especially ****** that is 6 to 20 % of the weight in carbon or black lead is preferred.

[0035]As a binder for holding the electrode compound used by this invention, kinds or these mixtures can be used for the polymer which has polysaccharide, thermoplastics, and rubber elasticity. As a desirable binder, starch, carboxymethyl cellulose, Cellulose, diacetyl cellulose, methyl cellulose, hydroxyethyl cellulose, Hydroxypropylcellulose, alginic acid Na, polyacrylic acid, Polyacrylic acid Na, polyvinyl phenol, polyvinyl methyl ether, Polyvinyl alcohol, a polyvinyl pyrrolidone, polyacrylamide, Water-soluble polymer, such as polyhydroxy (meta) acrylate and a styrene maleic acid copolymer, Polyvinylchloride, polytetra FURURORO ethylene, polyvinylidene fluoride, A tetrafluoroethylene-hexafluoropropylene copolymer, a vinylidene fluoride tetrafluoroethylene-hexafluoropropylene copolymer, Polyethylene, polypropylene, an ethylene-propylene-diene terpolymer (EPDM), The acrylic ester copolymer (meta), acrylic acid (meta) ester acrylonitrile copolymer containing acrylic ester (meta), such as sulfonation EPDM, polyvinyl-acetal resin, a methylmetaacrylate, and 2-ethylhexyl acrylate, The polyvinyl ester copolymer containing vinyl ester, such as vinyl acetate, A styrene butadiene copolymer, an acrylonitrile butadiene copolymer, Polybutadiene, neoprene rubber, fluorocarbon rubber, polyethylene oxide, An emulsion (latex) or suspension, such as polyester polyurethane resin, polyether polyurethane resin, polycarbonate polyurethane resin, polyester resin, phenol resin, and an epoxy resin, can be mentioned. Latex of a polyacrylic ester system, carboxymethyl cellulose, polytetrafluoroethylene, and polyvinylidene fluoride are especially preferred. It can be independent, or it can mix and these binders can be used. If too large [when there are few additions of the binder, the holding power and cohesive force of an electrode compound are weak, and cycle nature is bad again, and], an electrode body product will increase, electrode unit volume or the capacity per unit weight will decrease, conductivity falls further and capacity decreases. Although the addition in particular of a binder is not limited, its 1 to 30 % of the weight is especially preferred, and its 2 to 10 % of the weight is preferred.

[0036]It is preferred to perform adjustment of the negative electrode mixture of this invention or a positive electrode mixture paste by a drainage system. Adjustment of mixture paste mixes an active material and a conducting agent first, it adds a binder (the suspension of resin powder, or emulsion (latex)-like thing), and water, and kneading mixing is carried out, Then, it can carry out by stirring mixers, such as a mixer, a

homogenizer, dissolver, a planetary mixer, a paint shaker, and a sand mill, and a dispersion machine distributing. On a charge collector, the mixture paste of the positive active material and negative electrode active material which were adjusted is applied (coat) dried and compressed, and is mainly used. Although spreading can be performed by various methods, the reverse roll method, the Dailekh trawl method, the braid method, the knife method, the extrusion method, the curtain method, the photogravure method, the bar method, a dip method, and the squeeze method can be mentioned, for example. The braid method, the knife method, and the extrusion method are preferred. As for spreading, it is preferred to carry out the speed for 0.1-100-m/. Under the present circumstances, according to the liquid nature of mixture paste, and drying property, the surface state of a good coating layer can be acquired by selecting the above-mentioned coating method. Although the thickness, length, and width of the coating layer are decided with the size of a cell, the thickness of a coating layer is in the state compressed after desiccation, and especially its 1-2000 micrometers are preferred.

[0037]the method generally adopted can be used as a pellet, or the desiccation for the water removal of a sheet or a dehydration method -- a hot wind, a vacuum, infrared rays, far-infrared rays, an electron beam, and a damp wind -- it can be independent, or it can combine and can use. The temperature of the range of 80-350 ** is preferred, and is especially preferred. [of the range which is 100-250 **] 2000 ppm or less of water content are preferred by the whole cell, and it is preferred to use 500 ppm or less in positive electrode mixture, negative electrode mixture, or an electrolysis solution, respectively in respect of charging and discharging cycle nature.

[0038]Although the compression of a sheet shaped electrode compound can use the pressing method generally adopted, a die-press method and the calendar pressing method are especially preferred. Although press pressure in particular is not limited, 10 kg/cm^2 - 3 t/cm^2 are preferred. As for the pressing speed of the calendar pressing method, the amount of 0.1-50-m/is desirable. Room temperature -200 ** of press temperature is preferred.

[0039]the base material, i.e., the charge collector, of an anode and a negative electrode which can be used by this invention. As construction material, it is aluminum, stainless steel, nickel, titanium, or these alloys at an anode, and is copper, stainless steel, nickel, titanium, or these alloys at a negative electrode, and they are foil, an expanded metal, a punching metal, and a wire gauze as a gestalt. In particular, to an anode, copper foil is [aluminium foil and a negative electrode] preferred.

[0040]The separator which can be used by this invention has the large degree of ion permeation, to have a predetermined mechanical strength, and what is necessary is just an insulating thin film, and as construction material, Olefin system polymer, fluorine system polymer, cellulose type polymer, polyimide, nylon, glass fiber, and an alumina fiber are used, and a nonwoven fabric, textile fabrics, and a microporous film are used as a gestalt. In particular, as construction material, the mixture of polypropylene, polyethylene, polypropylene, the mixture of polyethylene and polypropylene, and Teflon and the mixture of polyethylene and Teflon are preferred, and what is a microporous film as a gestalt is preferred. In particular, the 5-50-micrometer-thick microporous film whose aperture is 0.01-1 micrometer is preferred.

[0041]The shape of a cell is applicable to both a button, coin a sheet a cylinder an angle, etc. A cell inserts in a battery can the electrode wound with the pellet, the sheet shaped, or the separator, electrically connects an electrode with a can, and pours in, obturates and forms an electrolysis solution. At this time, a safety valve can be used as an obturation board. In order to guarantee the safety of a cell, it is preferred to use a PTC element.

[0042]The steel board with which the closed-end cell sheathing can which can be used by this invention performed the nickel plate as construction material, a stainless steel plate (SUS304, SUS304L, and SUS304N.) It is SUS316, SUS316L, SUS430, SUS444 grade, the stainless steel plate (same as the above) that performed the nickel plate, aluminum or its alloy, nickel, titanium, and copper, and is round shape tubed, ellipse form tubed one, square tubed, and rectangle tubed as shape. Especially when an armor can serves as a negative pole terminal, a stainless steel plate and the steel board which performed the nickel plate are preferred, and when an armor can serves as a positive pole terminal, a stainless steel plate, aluminum, or its alloy is preferred.

[0043]The mixture electrode of this sheet shaped is rolled or folded, is inserted in a can, electrically connects a sheet with a can, pours in an electrolysis solution, and forms a battery can using an obturation board. At this time, a safety valve can be used as an obturation board. It may be equipped with various safety elements known from the former besides a safety valve. For example, a fuse, bimetal, a PTC element, etc. are used as an overcurrent-protection element. The method of making a cut in a battery can other than a safety valve, the

gasket crack method, or the obturation board crack method can be used as a measure against the internal pressure rise of a battery can. The circuit which built the surcharge and the measure against overdischarge into the charge machine may be made to provide.

[0044]Although an electrolysis solution may pour in the whole quantity at once, it is preferred to carry out by dividing into two or more steps. When dividing and pouring into two or more steps, the presentation (after pouring in the solution which dissolved lithium salt in the nonaqueous solvent or the nonaqueous solvent, the solution which dissolved lithium salt in the nonaqueous solvent or nonaqueous solvent whose viscosity is higher than said solvent is poured in) which is different also by the same presentation may be sufficient as each liquid. a shortening of the injection time of an electrolysis solution, etc. sake -- a battery can -- decompression (desirable -- 500-1 --) [torr and] Although it may perform carrying out 400-10 torr more preferably, or applying a centrifugal force and an ultrasonic wave to a battery can, it is preferred not to make too much the carbon dioxide which was dissolved into the electrolysis solution in any case diffuse. When it pours in especially using decompression, it is preferred to use a method of making carbon dioxide content gas contact after pouring in like the account of the point.

[0045]Metal and an alloy with electrical conductivity can be used for a can or a lead board. For example, metal or those alloys, such as iron, nickel, titanium, chromium, molybdenum, copper, and aluminum, are used. A publicly known method (electric welding of an example, a direct current, or exchange, laser welding, ultrasonic welding) can be used for the welding process of a cap, a can, a sheet, and a lead board. The compound and mixture which are known from the former, such as asphalt, can be used for the sealing compound for obturation.

[0046]As construction material, they are olefin system polymer, fluorine system polymer, cellulose type polymer, polyimide, and polyamide, from organic solvent-proof nature and low-water-flow part permeability, the gasket which can be used by this invention has preferred olefin system polymer, and especially its polymer of a propylene subject is preferred. It is preferred that it is block copolymerization polymer of propylene and ethylene.

[0047]The cell of this invention is covered with a sheathing material if needed. As a sheathing material, there are heat-shrinkable tubing, adhesive tape, a metallic film, paper, cloth, a paint, a plastic case, etc. The portion of the exterior discolored with heat in part at least is provided, and it may be made for a heat history in use to be known. The cell of this invention constructs two or more in series and/or in parallel if needed, and is stored by the battery pack. A safety circuit (circuit with the function which intercepts current if the voltage of each cell and/or the whole cell group, temperature, current, etc. are monitored and it is required) besides safety elements, such as a right temperature coefficient resistor, a thermal cutout, a fuse, and/or a current cutoff element, may be established in a battery pack. The anode of each cell and a negative pole terminal, the whole cell group and the temperature detection terminals of each cell, the current detection terminal of the whole cell group, etc. can also be provided in a battery pack as an external terminal in addition to the anode and negative pole terminal of the whole cell group. Voltage conversion circuits (DC-DC converter etc.) may be built in a battery pack. It may fix by welding a lead board, and connection of each cell may be fixed so that it can detach and attach easily with a socket etc. Display functions, such as battery remaining capacity, existence of charge, and a use count, may be provided in a battery pack.

[0048]The cell of this invention is used for various apparatus. Especially A video movie, a portable videocassette recorder with a built-in monitor, a movie camera with a built-in monitor, It is preferred to be used for a compact camera, a single-lens reflex camera, a disposable camera, a notebook sized personal computer, a note type word processor, an electronic notebook, a cellular phone, a cordless telephone, a mustached camber, a power tool, an electric mixer, a car, etc.

[0049]

[Example]Although an example is raised to below and this invention is explained in more detail, unless the main point of an invention is exceeded, this invention is not limited to an example.

[0050][The example of creation of a positive electrode mixture paste]

Positive active material; $LiCoO_2$ (what put into the alumina crucible what was mixed with lithium carbonate and a tricobalt tetroxide by the mole ratio of 3:2, was calcinated at 900 ** for 8 hours, and was cracked at it at the speed of 2 more **/m at the temperature of temperature-up Perilla frutescens (L.) Britton var. crispa (Thunb.) Decne. after carrying out temperature up to 750 ** and carrying out temporary quenching to it at 2 **/m for 4 hours, among the air and.) The electric conductivity of dispersion liquid when centriole child size 5micrometer and the washing article 50g are distributed in 100 ml of water 0.6 mS/m, The specific surface area according [

pH] to 10.1 and a nitrogen absorption method 0.42-m^2/g 200 g and 10 g of acetylene black, Continuously the water dispersed matter (50 % of the weight of solids concentration) of 2-ethylhexyl acrylate, acrylic acid, and the copolymer of acrylonitrile as a binder with a homogenizer 8 g, [mix and] 60 g was added, kneading mixing of the carboxymethyl cellulose solution of 2 % of the weight of concentration was carried out, further, 50 g was added, stirring mixing of the water was carried out with the homogenizer, and the positive electrode mixture paste was created.

[The example of creation of a negative electrode mixture paste]

Negative-electrode-active-material A;$SnGe_{0.1}B_{0.5}P_{0.58}Mg_{0.1}K_{0.1}O_{3.35}$ (6.7 g of tin protoxide) The pyrophoric acid tin 10.3g, 1.7 g of boron oxide, the potassium carbonate 0.7g, Dry blending of the magnesium oxide 0.4g and the diacid-ized germanium 1.0g is carried out, Put into the crucible made from alumina and temperature up is carried out to 1000 ** by a part for bottom 15 **/of argon atmosphere, After calcinating at 1100 ** for 12 hours, what was lowered even to the room temperature by a part for 10 **/, and was taken out from the firing furnace is collected, What was ground with the jet mill, the mean particle diameter of 4.5 micrometers, and the volume fraction of a particle of 1 micrometer or less 0.1% or less, It is a thing which has a broadcloth peak which has the peak near 28 degree with 2theta value in the X-ray diffraction method using CuK alpha rays, The crystalline diffraction line was not looked at by not less than 40 degrees 70 degrees or less with 2theta value. 200 g, What was mixed with 30 g of conducting agents (artificial graphite) and a homogenizer, added the carboxymethyl cellulose solution 50g of 2 % of the weight of concentration and the polyvinylidene fluoride 10g as a binder further, and was mixed, and 30g of water were added, kneading mixing was carried out further, and the negative electrode mixture paste was created.

[0051][Creation of an anode and a negative pole electrode sheet] The positive electrode mixture paste created above by a braid coating machine to both sides of a 30-micrometer-thick aluminium foil charge collector. After having applied so that the thickness of the sheet after coverage 400 g/m^2 and compression might be set to 280 micrometers, and drying, compression molding was carried out with the roller press machine, it judged in the predetermined size, and the band-like positive electrode sheet was created. Furthermore, drying desiccation was enough carried out with the far infrared heater all over the dry box (dew point; dry air of -50 ** or less **), and the positive electrode sheet was created. Similarly, the negative electrode mixture paste was applied to a 20-micrometer copper foil charge collector, and the thickness of the sheet after coverage 70 g/m^2 and compression created the negative electrode sheet which is 90 micrometers by the same method as the above-mentioned positive electrode sheet creation.

[The example of electrolysis solution adjustment] By argon atmosphere, 65.3 g of diethyl carbonate was put into the polypropylene container of a 200-cc thin mouth, and 22.2 g of ethylene carbonate [a little] was dissolved every, taking care that solution temperature does not exceed 30 ** to this. Next, it dissolved in the above-mentioned polypropylene container every in small quantities in order, respectively, being careful of 0.4 g $LiBF_4$ and 12.1-g $LiPF_6$ for solution temperature not to exceed 30 **. The obtained electrolysis solution was a water-white fluid by specific gravity 1.135. Moisture was 18 ppm. (It measures with the Carl Phi Shah water measurement device) The carbon dioxide levels at this time were less than 0.001 mol/l. again.

[The example of creation of a cylinder cell] It laminated in order of the positive electrode sheet, the separator made from a microporous polypropylene film, the negative electrode sheet, and the separator, and this was wound spirally. It stored to the iron closed-end cylindrical battery can which performed the nickel plate which serves this winding body as a negative pole terminal. the battery lid which pours in the appointed electrolysis solution into a battery can in a pouring-in booth, and has a positive pole terminal in an obturation booth further -- a gasket -- passing -- it obturated in total and the cylindrical cell was created.

[0052]It was made to contact by predetermined mind/liquor to wood ratio shown in the air which contains carbon dioxide in Example 1 - the electrolysis solution of 3 above using an aeration pipe, and Table 1. This electrolysis solution was used and the cylinder cell was created according to the above-mentioned procedure.

[0053]

carbon dioxide in an electrolysis solution Table 1 Gas used . Gas-liquid ratio Carbon dioxide levels Number Carbon dioxide content (volume/volume) mol / liter example 1 One Volume % 1000/1 0.006 Example 2 10 volume % 100/1 0.02 Example 3 99 volume % 100/1 0.05[0054]Example 4 electrolysis solution was put into the wide mouth container, and the whole container was put in in the pressure vessel, and in the pressure vessel, carbon dioxide content gas (99%) was introduced, and it pressurized to 3 atmospheres. The inside of a pressure vessel was returned to ordinary pressure, the electrolysis solution was taken out, and the cylinder cell was created according to the above-mentioned procedure.

It obturated, after neglecting it for 10 hours in the booth which circulated carbon dioxide content gas (99%) in the state before obturating the cylindrical battery can which poured in example 5 electrolysis solution, and which has been winding body stored, and the cylinder cell was created.
It put in in the pressure vessel in the state before obturating the cylindrical battery can which poured in example 6 electrolysis solution and which has been winding body stored, and in the pressure vessel, carbon dioxide content gas (99%) was introduced, and it pressurized to 3 atmospheres. The inside of a pressure vessel was returned to ordinary pressure, the battery can was taken out, and the cylinder cell was created according to the above-mentioned procedure.
Carbon dioxide content gas (99%) was circulated in the example 7 obturation booth, cell obturation was performed in it, and the cylinder cell was created.
[0055]By the same method as comparative example 1 Example 1, pouring in and obturation were performed by the usual method using the electrolysis solution which does not perform contact operation with carbon dioxide content gas, and the cylinder cell was created.
It changed into the comparative example 2 - tetroxide system negative electrode active material, the negative electrode sheet was created by the same method as creation of said negative electrode sheet using the carbon system active material (graphite powder), and the cylindrical cell was created, using respectively the electrolysis solution which performed the same operation as Examples 1-3.
It changed into comparative example pentoxide system negative electrode active material, and the negative electrode sheet was created by the same method as creation of said negative electrode sheet using the carbon system active material (graphite powder), pouring in and obturation were performed by the usual method using the electrolysis solution which does not perform contact operation with carbon dioxide content gas like the comparative example 1, and the cylinder cell was created.
Except making the volume fraction of 1 micrometer or less of detailed powder of Example 8 - the 10 negative electrode active material A into 3%, the negative electrode active material B was made like A, and the same operation and experiment as Examples 1-3 were conducted.
The same experiment as the comparative example 1 was conducted using the comparative example 6 negative electrode active material B.
[0056]About the cell created by the above-mentioned method, charge and discharge were carried out on condition of current density 5 mA/cm^2, the charge final voltage 4.1V, and the discharge final voltage 2.8V, and service capacity and a cycle life were searched for. The ratio and cycle nature (300th capacity to the 1st charge and discharge comparatively) of capacity (Wh) of each cell are shown in Table 2.
[0057]
Table 2 It is an experimental run number as a result of an experiment. Carbon dioxide introduction Negative electrode active material Initial capacity Cycle nature (%)
Example 1 Front [pour] liquid Oxide A 100 83 Examples 2. Front [pour] liquid Oxide A 101 85 Examples 3. Front [pour] liquid Oxide A 99 88 Examples 4. Front [pour] liquid Oxide A 99 91 Examples 5. Before a hole for seal after clysis Oxide A 100 85 Examples 6. Before a hole for seal after clysis Oxide A 98 89 Examples 7. time of obturation Oxide A 98 the 88 comparative examples 1 -- nothing . oxide A 100 the 74 comparative examples 2 -- front [pour] liquid . carbon system 80 the 78 comparative examples 3 -- front [pour] liquid Carbon system . 81 79 comparative-example 4 Front [pour] liquid Carbon system 80 80 comparative-example 5 Nothing Carbon system 79 75 example 8 Front [pour] liquid Oxide B 100 80 example 9 Front [pour] liquid Oxide B 101 83 example 10 Front [pour] liquid Oxide B 99 87 comparative-example 6 Nothing Oxide B 100 69[0058]The cell which uses the oxide stock negative electrode active material of this invention has large capacity to the cell which uses carbon system negative electrode active material, and cycle nature of the cell which performed contact operation of an electrolysis solution and carbon dioxide content gas is improving further.
An improvement rate is larger than what used carbon system negative electrode active material.

[0059]
[Effect of the Invention]Including the material which becomes a negative electrode from an amorphous charcogen compound and/or an amorphous oxide like this invention, by making carbon dioxide contain in nonaqueous electrolyte, it has the outstanding charging and discharging characteristic, and a nonaqueous electrolyte secondary battery with still less degradation of the service capacity by charge-and-discharge repetition can be obtained.